

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : B44B 7/00, H01J 37/305	A1	(11) International Publication Number: WO 98/52774 (43) International Publication Date: 26 November 1998 (26.11.98)
(21) International Application Number: PCT/GB98/01497 (22) International Filing Date: 22 May 1998 (22.05.98) (30) Priority Data: 9710738.7 23 May 1997 (23.05.97) GB 9727365.0 24 December 1997 (24.12.97) GB (71) Applicant (for all designated States except US): GERSAN ESTABLISHMENT [LU/LI]; Aeulestrasse 5, FL-9490 Vaduz (LI). (72) Inventors; and (75) Inventors/Applicants (for US only): SMITH, James, Gordon, Charters [GB/GB]; 5 Glynswood, High Wycombe, Buckinghamshire HP13 5QL (GB). STEWART, Andrew, David, Garry [GB/GB]; The Old Rectory, Ashampstead, Reading, Berkshire RG8 8SH (GB). (74) Agent: WALDREN, Robin, Michael; Marks & Clerk, 57-60 Lincoln's Inn Fields, London WC2A 3LS (GB).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: DIAMOND MARKING (57) Abstract <p>An information mark invisible to the naked eye is applied to the polished facet of a diamond gemstone by coating the diamond gemstone surface with an electrically conductive layer so as to prevent the diamond becoming charged, forming the mark with a focused ion beam, and cleaning the diamond surface with a powerful oxidizing agent to reveal a mark having an appropriate depth, which does not detrimentally affect the clarity or colour grade of the diamond.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

Diamond Marking

Background to the Invention

The present invention relates to a method of marking a surface of a diamond or gemstone. The mark may be any mark, but the invention is particularly though not exclusively directed to applying an information mark to the diamond or gemstone. The diamond may be for instance an industrial diamond such as a wire-drawing die or diamond optical component, though the invention is of particular interest in marking gemstone diamonds, for instance for applying a mark which is invisible to the naked eye or invisible to the eye using a x10 loupe, when the mark can be applied to a polished facet of the gemstone without detracting from its clarity or colour grade. When a loupe is used, the visibility is assessed under the internationally accepted conditions for clarity grading, i.e. using a 10x magnifying achromatic, aplanatic loupe under normal light, this being a white diffuse light, not a spot light. The marks can be used to uniquely identify the gemstone by a serial number or as a brand or quality mark. In general, the mark should be capable of being viewed under suitable magnification and viewing conditions, and, if applied to a gemstone, should not detract from the value or appearance of the stone and should preferably not exhibit blackening.

There is a detailed description of the nature of the marks that can be applied in WO 97/03846, in which the marks are applied by irradiating a diamond gemstone with ultraviolet laser radiation using a projection mask.

It is generally desirable to produce marks of improved resolution and to reduce the time required to apply the marks so that for instance serial numbers can be applied.

SUBSTITUTE SHEET (RULE 26)

The Invention

According to a first aspect of the present invention, the surface of a diamond or gemstone is marked with a focused ion beam, the mark being invisible to the naked eye. The invention extends to a diamond or gemstone which has been marked by the method of the invention, and to apparatus for carrying out the method.

The marking can be carried out by direct writing on the diamond or gemstone surface with a focused ion beam. Typically Gallium ions are used, but a beam of other suitable ions may alternatively be used. By limiting the dose, sputtering of carbon atoms can be substantially avoided, sputtering causing direct material removal; this enables a mark to be applied with a controlled depth and good resolution. By limiting the dose, and providing there is sufficient dose, the incident ions cause disordering of the crystal lattice. In the case of diamond, this converts the diamond to a graphite-like or other non-diamond structure that can then be cleaned, e.g. using an acid or potassium nitrate dissolved in acid, to leave a shallow mark say not less than 10 nm deep and/or not more than 70 nm deep, more preferably say not less than 20 nm deep and/or not more than about 50 nm deep, typically about 30 nm deep, with no evidence of blackening. Plasma etching may be used as an alternative to acid cleaning.

However, in a preferred embodiment, the disordered layer produced on the diamond or gemstone by the ion beam is removed by means of a powerful oxidizing agent, such as molten potassium nitrate. This method allows a mark to be produced at a lower dose and therefore in less time at a given beam current. Alternatively, a lower beam current, giving a smaller spot size may be used to produce marks with higher resolution features, such as diffraction gratings.

The depth of the lattice disordering is determined by the range of the ions. For 50 keV Gallium, this range is about 30 nm. The minimum dose may be as low as $10^{13}/\text{cm}^2$, but

is preferably about $10^{14}/\text{cm}^2$ to $10^{15}/\text{cm}^2$. However, good marks can be applied with a fairly modest dose, the preferred maximum dose being about $10^{16}/\text{cm}^2$ or even up to about $10^{17}/\text{cm}^2$. However, the dose depends upon the ions being used and their energy (as measured in keV). The ion beam dose is a total number of incident ions per unit area at the sample surface, during the marking. The beam current may be about 1 nA, and the beam energy not less than about 10 keV or about 30 keV and/or not greater than about 100 keV or about 50 keV.

It has been found that if depth of mark is plotted against ion beam dose for a series of different beam energies, there is an increase of depth of mark with increasing beam energy. Characteristics of the mark may be optimised by selecting from the dose/energy combinations which will result in the desired depth of mark.

The region to be marked and/or the surrounding area may be coated with an electrically-conducting layer, for instance gold, prior to forming the mark, so that an electrical connection can be provided before marking with the ion beam, to prevent charging. The thickness of the gold, or other, coating alters the variation of depth of mark with beam energy and dose, and may thus be chosen to optimise the mark produced.

Other suitable methods to reduce charging may be used. One method is to irradiate the region to be marked with a low energy ion beam, e.g. about 3 to about 10 keV, prior to forming the mark, to modify the diamond surface to cause it to become electrically conductive, the electrical connection being made to that region. In a preferred embodiment, the ion beam used for marking may be used in conjunction with a charge neutralising device, such as an electron flood gun, such as that described in US patent specification number US-4639301, to prevent charging of the diamond surface.

In accordance with a second aspect of the present invention, there is provided a method of marking the surface of a diamond or gemstone, comprising the steps of irradiating at

least a portion of said diamond or gemstone to form a damaged or crystal lattice disordered layer thereon, and removing said disordered layer using an oxidizing agent.

A further advantage of the second aspect of the present invention over acid-cleaning is that no acid fumes are produced and also that spent acid does not have to be disposed of, thereby improving the safety of the process as well as offering environmental and economic benefits.

The oxidizing agent is preferably molten potassium nitrate. The diamond or gemstone is preferably covered with potassium nitrate and heated to a temperature of around 380-550 Centigrade for a period of between a few minutes and several hours, preferably approximately one hour.

However, other suitable powerful oxidizing agents include molten compounds such as alkali metal salts. Suitable compounds may be in the form X_nY_m where the group X may be Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , or other cation, and the group Y may be OH^- , NO_3^- , O_2^{2-} , O^{2-} , CO_3^{2-} or other anion; the integers n and m being used to maintain charge balance. Mixtures of compounds may be used. Air or other oxygen-containing compounds may also be present.

The use of such oxidizing agents to remove a disordered layer allows a mark of a desired depth to be produced using a relatively low dose of ions.

In a preferred embodiment, the diamond or gemstone is irradiated with an ion beam as in the first aspect of the present invention, and most preferably a Gallium ion beam. The preferred embodiment of the method of the second aspect resulting in a remarkably efficient process, with each incident Gallium ion ultimately resulting in the removal of approximately 2,700 carbon atoms. In most materials other than diamond, this figure would be around 1-10.

It is this property of diamond that allows the relatively large structures such as alphanumeric characters covering an area of 0.43 mm by 0.16 mm to be machined in a reasonably economic time of about 10 seconds.

The method of the present invention may also be used to mark the surface of a synthetic gemstone, such as the silicon carbide gemstones described in WO 97/09470.

Example

A diamond gemstone is mounted in a suitable holder and a facet is coated with a layer of gold. The sample is placed in a vacuum chamber equipped with a focused ion beam source such as supplied by FEI or Micrion, the holder making an electrical connection to the gold layer to prevent the diamond becoming charged. Using a focused beam with a raster scan or similar to scan the beam for instance with electrostatic deflection (as an alternative, the diamond may be moved, but this is less practical), a mark is written on the diamond facet with ions to a dose of 10^{15} to $10^{16}/\text{cm}^2$, the ion source being Gallium, the beam current 1 nA and the beam energy 30 to 50 keV. The sample is removed from the vacuum chamber and acid cleaned to remove the disordered layer and the gold layer. There is a shallow mark typically about 30 nm deep, with no evidence of blackening.

The present invention has been described above purely by way of example, and modifications can be made within the spirit of the invention, which extends to the equivalents of the features described. The invention also consists in any individual features described or implicit herein or shown or implicit in the drawings or any combination of any such features or any generalisation of any such features or combination.

CLAIMS:

1. A method of marking the surface of a gemstone, comprising forming a mark with a focused ion beam, wherein the mark is invisible to the naked eye.
2. The method of Claim 1, wherein the gemstone is a diamond.
3. The method of Claim 1, wherein the gemstone is a silicon carbide gemstone.
4. A method of marking the surface of a gemstone, comprising the steps of irradiating at least a portion of said gemstone to form a disordered layer thereon, and removing said disordered layer using an oxidizing agent.
5. The method of Claim 4, wherein the gemstone is a diamond.
6. The method of Claim 4, wherein the gemstone is a silicon carbide gemstone.
7. The method of any one of Claims 4 to 6, wherein the gemstone is irradiated using an ion beam.
8. The method of Claim 7, wherein the gemstone is irradiated using a focused ion beam.
9. The method of any one of Claims 1 to 3, wherein the surface of the gemstone is irradiated by means of said focused ion beam to form a disordered layer thereon, and said disordered layer is removed using an acid.
10. A method of marking the surface of a diamond, comprising forming a mark with a focused ion beam, wherein the mark is invisible to the naked eye.

11. The method of Claim 10, wherein the surface of the diamond is irradiated by means of said focused ion beam to form a disordered layer thereon, and said disordered layer is removed using an acid.
12. A method of marking the surface of a diamond, comprising the steps of irradiating at least a portion of the diamond to form a disordered layer thereon, and removing said disordered layer using an oxidizing agent.
13. The method of claim 12, wherein the diamond is irradiated using an ion beam.
14. The method of claim 13, wherein the diamond is irradiated using a focused ion beam.
15. The method of Claim 9 or Claim 11, wherein said disordered layer is removed using an oxidising agent dissolved in acid.
16. The method of Claim 15, wherein said disordered layer is removed using potassium nitrate dissolved in acid.
17. The method of any one of Claims 1 to 3, 7 to 11, or 13 or 14 wherein the mark is formed at a dose of not more than about $10^{17}/\text{cm}^2$.
18. The method of any one of Claims 1 to 3, 7 to 11, or 13 or 14 wherein the mark is formed at a dose of not more than about $10^{16}/\text{cm}^2$.
19. The method of any one of Claims 1 to 3, 7 to 11, 13, 14, 17 or 18, wherein the mark is formed at a dose of not more than about $10^{15}/\text{cm}^2$.
20. The method of any one of Claims 1 to 3, 7 to 11, 13, 14, or 17 to 19, wherein the mark is formed at a dose of not less than about $10^{14}/\text{cm}^2$.

21. The method of any one of Claims 1 to 3, 7 to 11, 13, 14 or 17 to 19, wherein the mark is formed at a dose of not less than about $10^{13}/\text{cm}^2$.
22. The method of any one of Claims 1 to 3, 7 to 11, 13, 14 or 17 to 21, wherein the beam current is about 1 nA.
23. The method of any one of Claims 1 to 3, 7 to 11, 13, 14 or 17 to 21, wherein the beam current is about 0.5 nA.
24. The method of any one of Claims 1 to 3, 7 to 11, 13, 14 or 17 to 21, wherein the beam current is about 0.1 nA.
25. The method of any one of Claims 1 to 3, 7 to 11, 13, 14 or 17 to 24, wherein the beam energy is about 10 to about 100 keV.
26. The method of Claim 25, wherein the beam energy is about 30 keV to about 50 keV.
27. The method of any one of Claims 1 to 3, 7 to 11, 13, 14 or 17 to 26, wherein the ion beam is a Gallium ion beam.
28. The method of any of the proceeding Claims, wherein the depth of the mark is about 10 to about 70 nm.
29. The method of any of the preceding Claims, wherein the depth of the mark is about 20 to about 50 nm.
30. The method of any of the preceding Claims, wherein the depth of the mark is about 20 to about 30 nm.

31. The method of any one of Claims 1 to 3, 7 to 11, 13, 14 or 17 to 30, including coating said surface with an electrically-conductive layer prior to forming the mark.
32. The method of Claim 27, wherein the layer is gold.
33. The method of any of Claims 1 to 3, 7 to 11, 13, 14 or 17 to 30, wherein the region to be marked is irradiated with a low energy ion beam prior to forming the mark, to modify the diamond surface to cause it to become electrically conductive.
34. The method of Claims 1 to 3, 7 to 11, 13, 14 or 17 to 30, wherein the region to be marked is simultaneously irradiated using a charge neutralising device.
35. The method of Claim 33, wherein the energy of said low energy ion beam is about 3 to 10 keV.
36. The method of any of the preceding Claims, wherein the mark is an information mark.
37. The method of any of the preceding Claims, wherein the mark is invisible to the eye using a x10 loupe.
38. The method of any of Claims 4 to 6 or 12 to 14, wherein the mark is invisible to the naked eye.
39. The method of any of the preceding Claims, wherein the mark is applied to a polished facet of a gemstone.
40. The method of any one of Claims 1 to 3 or 10, wherein the surface of the diamond or gemstone is irradiated by means of said focused ion beam to form a disordered layer thereon, and said disordered layer is removed using an oxidizing agent.

41. The method of Claim 4 or 40, wherein the oxidizing agent is potassium nitrate.
42. The method of Claim 4, 15 or 41, wherein the oxidizing agent is at least one compound in the form X_nY_m where the group X is Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , or other cation, and the group Y is OH^- , NO_3^- , O_2^{2-} , O^{2-} , CO_3^{2-} or other anion; the integers n and m being used to maintain charge balance.
43. The method according to any preceding claim comprising the steps of irradiating at least a portion of a gemstone with an ion beam to form a disordered layer thereon and removing said disordered layer by substantially covering the disordered layer with molten potassium nitrate.
44. The method according to any preceding claim comprising the steps of irradiating at least a portion of a diamond with an ion beam to form a disordered layer thereon and removing said disordered layer by substantially covering the disordered layer with molten potassium nitrate.
45. The method of Claim 42 or Claim 43, wherein the temperature of said gemstone or diamond and molten potassium nitrate is maintained for approximately one hour.
46. A method of marking the surface of a gemstone, substantially as herein described in the foregoing Examples.
47. A method of marking the surface of a diamond, substantially as herein described in the foregoing Examples.
48. A gemstone which has been marked by the method of any of the preceding Claims.
49. A diamond which has been marked by the method of any of the preceding Claims.

50. A silicon carbide gemstone which has been marked by the method of any of the preceding claims.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 98/01497

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B44B7/00 H01J37/305

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B23K B44B C30B G03F H01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 425 769 A (M. HAKOUNE) 17 January 1984	1-3, 10, 36-38, 46-49
Y	see column 1, line 55 - column 4, line 2 see column 6, line 3	7-9, 11, 13-16, 40, 41, 43-45 17-21, 31
A	---	---

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"Δ" document member of the same patent family

Date of the actual completion of the international search

18 September 1998

Date of mailing of the international search report

24/09/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

Moet, H

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 98/01497

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 467 172 A (J. EHRENWALD) 21 August 1984 see column 2, line 65 - line 68 see column 5, line 1 - line 5 see column 5, line 31 - line 40	4-6, 12, 36-39
Y		7-9, 11, 13-16, 40, 41, 43-45
A	WO 97 09470 A (C3 INC) 13 March 1997 cited in the application see page 1, line 4 - line 6	3, 6
A	EP 0 480 394 A (SUMITOMO ELECTRIC INDUSTRIES) 15 April 1992 see page 9, line 2 - line 9	16, 41-45
A	US 4 200 506 A (G.A.M. DRESCHOFF ET AL) 29 April 1980 see the whole document	17-21
A	US 4 184 079 A (J.A. HUDSON ET AL) 15 January 1980 see the whole document	17-21
A	US 4 639 301 A (J.A. DOHERTY ET AL) 27 January 1987 cited in the application	17-35
A	EP 0 449 439 A (FUJITSU LTD) 2 October 1991 see page 6, line 5 - line 18; figures 1A-1D	31
A	US 4 117 301 A (J. GOEL ET AL) 26 September 1978 see column 3, line 35 - line 51 see column 4, line 36 - line 59; figures 1, 3, 7	32

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 98/01497

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
US 4425769	A	17-01-1984	BE 888714 A		28-08-1981
			EP 0064780 A		17-11-1982
US 4467172	A	21-08-1984	BE 898023 A		15-02-1984
WO 9709470	A	13-03-1997	US 5762896 A		09-06-1998
			AU 6902696 A		27-03-1997
			EP 0853690 A		22-07-1998
			US 5723391 A		03-03-1998
EP 480394	A	15-04-1992	JP 4240007 A		27-08-1992
			JP 2557560 B		27-11-1996
			JP 4146007 A		20-05-1992
			JP 4193406 A		13-07-1992
			DE 69107766 D		06-04-1995
			DE 69107766 T		29-06-1995
			KR 9504663 B		04-05-1995
			US 5178645 A		12-01-1993
US 4200506	A	29-04-1980	NONE		
US 4184079	A	15-01-1980	GB 1588445 A		23-04-1981
			BE 867492 A		18-09-1978
			CA 1100093 A		28-04-1981
			DE 2822723 A		07-12-1978
			FR 2391957 A		22-12-1978
			JP 1377373 C		08-05-1987
			JP 54013492 A		31-01-1979
			JP 61037205 B		22-08-1986
			NL 7805635 A		28-11-1978
US 4639301	A	27-01-1987	CA 1236223 A		03-05-1988
			EP 0200333 A		05-11-1986
			JP 1951580 C		28-07-1995
			JP 3138846 A		13-06-1991
			JP 1885910 C		22-11-1994
			JP 6003728 B		12-01-1994
			JP 61248346 A		05-11-1986
EP 449439	A	02-10-1991	JP 3261953 A		21-11-1991

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 98/01497

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 449439 A		KR 9402550 B	25-03-1994
US 4117301 A	26-09-1978	NONE	